CLAIMS

1. A method of forming a hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment: comprising:

- applying onto the substrate a mass of particles comprising hematite (Fe_2O_3) and one of:
  - (a) iron metal (Fe) with a weight ratio Fe/Fe_2O_3 of at least 0.3 and preferably no more than 2, in particular in the range from 0.8 to 1.4; or
  - (b) ferrous oxide (FeO) with a weight ratio FeO/Fe_2O_3 of at least 0.35 and preferably no more than 2.5, in particular in the range from 0.9 to 1.7; and
  - (c) iron metal (Fe) and ferrous oxide (FeO), with weight ratios Fe/Fe_2O_3 and FeO/Fe_2O_3 that are in pro rata with the ratios of (a) and (b);

and

- consolidating the applied mass of particles to form the hematite-containing protective layer by heat treating the mass of particles to:
  1) oxidise when present the iron metal (Fe) into ferrous oxide (FeO);
  2) sinter the hematite to form a porous sintered hematite matrix; and
  3) oxidise into hematite (Fe_2O_3) the ferrous oxide (FeO), present in the mass of particles as such and/or in the form of the oxidised iron metal, to fill the sintered hematite matrix.

2. The method of claim 1, wherein the mass of particles further comprises at least one additive selected from oxides of titanium, yttrium, ytterbium, tantalum, manganese, zinc, zirconium, cerium and nickel and/or heat-convertible precursors thereof.

3. The method of claim 2, wherein the additive(s) is/are present in the protective layer in an amount of 1 to 50 weight%, preferably 1 to 30 weight%, even more preferably 5 to 15 weight%.

4. The method of any preceding claim, wherein the protective layer further comprises one or more metals selected from Cu, Ag, Pd, Pt, Co, Cr, Al, Ga, Ge, Hf, In, Ir, Mo, Mn, Nb, Os, Re, Rh, Ru, Se, Si, Sn, Ti, V, W, Li, Ca, Ce and Nb and oxides thereof, which are added as such and/or as precursors to the mass of particles.

5. The method of claim 4, wherein the protective layer comprises said at least one metal and/or oxide thereof, in particular copper and/or copper oxide, in a total amount of 1 to 15 weight%, preferably from 1 to 10 weight, in particular from 1 to 5 weight%.

6. The method of any preceding claim, wherein the mass of particles is made of particles that are smaller than 75 micron, preferably smaller than 50 micron, in particular from 5 to 45 micron.

7. The method of any preceding claim, wherein the metal-based substrate is metallic, a ceramic, a cermet or metallic with an integral oxide layer.

8. The method of any preceding claim, wherein the metal-based substrate comprises at least one metal selected from chromium, cobalt, hafnium, iron, molybdenum, nickel, copper, niobium, platinum, silicon, tantalum, titanium, tungsten, vanadium, yttrium and zirconium.

9. The method of claim 8, wherein the metal-based substrate comprises an alloy of iron, in particular an iron alloy containing nickel and/or cobalt.

10. The method of claim any preceding claim, comprising oxidising the surface of a metallic substrate to form an integral anchorage layer thereon to which the protective layer is bonded by sintering during heat treatment, in particular an integral layer containing an oxide of iron and/or another metal, such as nickel, that is sintered during heat treatment with iron oxide from the mass of particles.

11. The method of any preceding claim, wherein the mass of particles is applied as a slurry onto the substrate.

12. The method of claim 11, wherein the slurry comprises an organic binder, in particular a binder selected from polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose, polyethylene glycol, ethylene glycol, hexanol, butyl benzyl phthalate and ammonium polymethacrylate.

13. The method of claim 11 or 12, wherein the slurry comprises an inorganic binder, in particular a colloid, such as a colloid selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia, indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thoria, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of colloids; and/or an inorganic polymer, such as a polymer selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide, gallium oxide, zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and thoria, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of inorganic polymers.

14. The method of claim 13, wherein the inorganic binder is sintered during the heat treatment with an oxide of an anchorage layer which is integral with the metal-based substrate to bind the protective layer to the metal-based substrate.

15. The method of any preceding claim, wherein the mass of particles is consolidated on the substrate by heat treatment at a temperature in the range from 800° to 1400°C, in particular from 850° to 1150°C.

16. The method of any preceding claim, wherein the mass of particles is consolidated on the substrate by heat treatment for 1 to 48 hours, in particular for 5 to 24 hours.

17. The method of any preceding claim, wherein the mass of particles is consolidated on the substrate by heat treatment in an atmosphere containing 10 to 100 mol% O_2.

18. The method of any preceding claim for manufacturing a component of a metal electrowinning cell, in particular an aluminium electrowinning cell, which during use is exposed to molten electrolyte and/or cell fumes and protected therefrom by said protective layer.

19. The method of claim 18 for manufacturing a current carrying anodic component, in particular an active anode structure or an anode stem.

20. The method of claim 18 for manufacturing a cover.

21. The method of any one of claims 18 to 20, comprising consolidating the mass of particles to form the protective layer by heat treating the cell component over the cell.

22. A method of electrowinning a metal, such as aluminium, comprising manufacturing a current-carrying anodic component protected by said protective layer as defined in claim 19, installing the anodic component in a molten electrolyte containing a dissolved salt of the metal to electrowin such as alumina, and passing an electrolysis current from the anodic component to a facing cathode in the molten electrolyte to evolve oxygen anodically and produce the metal cathodically.

23. The method of claim 22, wherein the electrolyte is a fluoride-based molten electrolyte, in particular containing fluorides of aluminium and sodium.

24. The method of claim 22 or 23, comprising maintaining the electrolyte at a temperature in the range from 800° to 960°C, in particular from 880° to 940°C.

25. The method of any one of claims 22 to 24, comprising maintaining in the electrolyte, particularly adjacent the anodic component, an alumina concentration which is at or close to saturation.

26. The method of any one of claims 22 to 25, comprising maintaining an amount of iron species in the electrolyte to inhibit dissolution of the protective layer of the anodic component.

27. A method of electrowinning a metal, such as aluminium, comprising manufacturing a cover protected by said protective layer as defined in claim 20, placing the cover over a metal electrowinning cell trough containing a molten electrolyte in which a salt of the metal to electrowin is dissolved, passing an electrolysis current in the molten electrolyte to evolve oxygen anodically and the metal cathodically, and confining electrolyte vapours and evolved oxygen within the cell trough by means of the protective layer of the cover.

28. A hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment, producible by the method of any one of claims 1 to 21, which is dense and at least substantially crack-free.

29. A cell for the electrowinning of a metal, such as aluminium, having at least one component that comprises a metal-based substrate covered with a hematite-containing protective layer as defined in claim 28.

30. A method of forming a hematite-containing body for use in a high temperature oxidising and/or corrosive environment: comprising:

- providing a mass of particles comprising hematite (Fe_2O_3) and one of:
  (a) iron metal (Fe) with a weight ratio Fe/Fe_2O_3 of at least 0.3 and preferably no more than 2, in particular in the range from 0.8 to 1.4; or
  (b) ferrous oxide (FeO) with a weight ratio FeO/Fe_2O_3 of at least 0.35 and preferably no more than 2.5, in particular in the range from 0.9 to 1.7; and
  (c) iron metal (Fe) and ferrous oxide (FeO), with weight ratios Fe/Fe_2O_3 and FeO/Fe_2O_3 that are in pro rata with the ratios of (a) and (b);
- shaping the mass of particles into the body;

and

- consolidating the body by heat treating the mass of particles to:
  1) oxidise when present the iron metal (Fe) into ferrous oxide (FeO);
  2) sinter the hematite to form a porous sintered hematite matrix; and
  3) oxidise into hematite (Fe_2O_3) the ferrous oxide (FeO), present in the mass of particles as such and/or in the form of the oxidised iron metal, to fill the sintered hematite matrix.

31. The method of claim 30, incorporating any of the features of claims 2 to 6 and/or wherein the mass of particles is provided in a slurry and consolidated as defined in any one of claims 12 to 13 or 15 to 17.

32. The method of claim 30 or 31, for manufacturing a component as defined in claims 18 to 20.